

AMENDMENTS TO THE CLAIMS

1. (Original) A catalyst system capable of catalysing the carbonylation of an ethylenically unsaturated compound, which system is obtainable by combining:

- a) a metal of Group VIB or Group VIIIB or a compound thereof,
- b) a bidentate phosphine, arsine, or stibine ligand, and
- c) an acid,

wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.

2. (Original) A catalyst system as claimed in claim 1 wherein the ratio of said ligand to said metal is in the range 5:1 to 750:1.

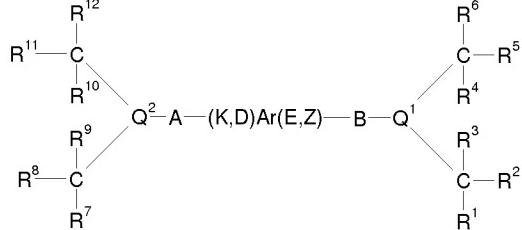
3. (Original) A catalyst system as claimed in claim 1 wherein the ratio of said ligand to said metal is in the range 10:1 to 500:1.

4. (Original) A catalyst system as claimed in claim 1 wherein the ratio of said ligand to said metal is in the range 20:1 to 40:1.

5. (Previously Presented) A catalyst system as claimed in claim 1 wherein the ratio of said acid to said ligand is in the range 5:1 to 95:1.

6. (Previously Presented) A catalyst system as claimed in claim 1 wherein the ratio of said acid to said ligand is in the range 20:1 to 40:1.

7. (Previously Presented) A catalyst system as claimed in claim 1 wherein the molar ratio of said acid to said metal is in the range 10:1 to 75000:1.
8. (Previously Presented) A catalyst system as claimed in claim 1 wherein the molar ratio of said acid to said metal is in the range 100:1 to 25000:1.
9. (Previously Presented) A catalyst system as claimed in claim 1 wherein the molar ratio of said acid to said metal is in the range 200:1 to 400:1.
10. (Previously Presented) A catalyst system as claimed in claim 1 wherein said ligand is a bidentate phosphine ligand.
11. (Previously Presented) A catalyst system as claimed in claim 1 wherein said ligand is of general formula (I)



(I)

wherein:

Ar is a bridging group comprising an optionally substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

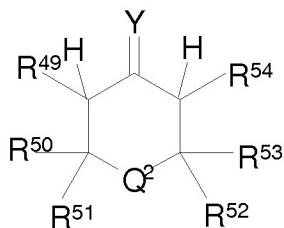
A and B each independently represent lower alkylene;

K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)R²⁵R²⁶, SR²⁷, C(O)SR²⁷, or -J-

$Q^3(CR^{13}(R^{14})(R^{15})CR^{16}(R^{17})(R^{18})$ where J represents lower alkylene; or two adjacent groups selected from K, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$;
 R^{13} to R^{18} each independently represent lower alkyl, aryl, or Het;
 R^{19} to R^{27} each independently represent hydrogen, lower alkyl, aryl or Het;
 R^1 to R^{12} each independently represent lower alkyl, aryl, or Het;
 Q^1 , Q^2 and Q^3 (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly, with preferably both Q^1 and Q^2 representing phosphorus, more preferably all of Q^1 , Q^2 and Q^3 (when present) representing phosphorus.

12. (Original) A catalyst system as claimed in claim 11 wherein at least one $(CR^xR^yR^z)$ group attached to Q^1 and/or Q^2 , i.e. $CR^1R^2R^3$, $CR^4R^5R^6$, $CR^7R^8R^9$, $CR^{10}R^{11}R^{12}$, $CR^{13}R^{14}R^{15}$, or $CR^{16}R^{17}R^{18}$, may instead be represented by the group (Ad) wherein:

Ad each independently represent an optionally substituted adamantyl or congressyl radical bonded to the phosphorous atom via any one of its tertiary carbon atoms, the said optional substitution being by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$; or if both $(CR^xR^yR^z)$ groups attached to either or both Q^1 and/or Q^2 , or Q^3 (if present) together with either Q^1 or Q^2 (or Q^3) as appropriate, form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or form a ring system of formula



wherein

R^{49} , and R^{54} , each independently represent hydrogen, lower alkyl or aryl;

R^{50} to R^{53} , when present, each independently represent hydrogen, lower alkyl, aryl or Het; and

Y represents oxygen, sulfur or $N-R^{55}$; and R^{55} , when present, represents hydrogen, lower alkyl or aryl.

13. (Previously Presented) A catalyst system as claimed in claim 11 wherein said ligand is represented as:



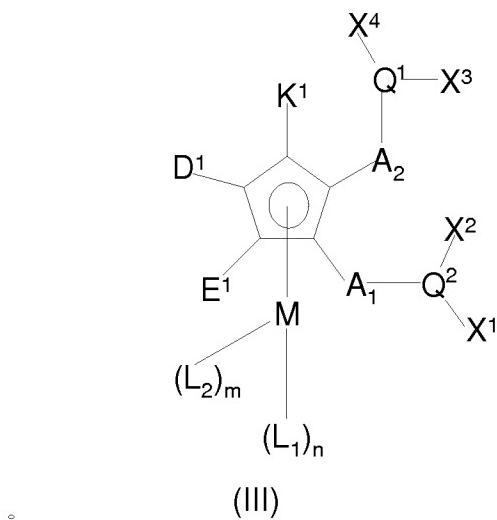
wherein Ar, A, B, K, D, E and Z, Q^1 , Q^2 , and Q^3 , and R^1 to R^{27} are as defined in claim 11 except that K, D, E and Z may represent $-J-Q^3(Ad)_W(CR^{13}(R^{14})(R^{15})_X$ instead of $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and Ad is as defined in claim 12,

$S \& U = 0, 1$ or 2 provided that $S + U \geq 1$;

$T \& V = 0, 1$ or 2 provided that $T + V \leq 3$;

$W \& X = 0, 1$ or 2 .

14. (Previously Presented) A catalyst system as claimed in claim 1 wherein said ligand is of general formula (III):



wherein:

A_1 and A_2 , and A_3 , A_4 and A_5 (when present), each independently represent lower alkylene;

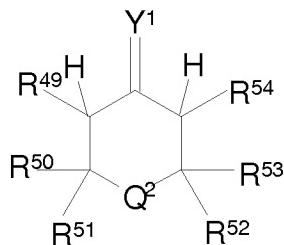
K^1 is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_3-Q^3(X^5)X^6$;

D^1 is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_4-Q^4(X^7)X^8$;

E^1 is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_5-Q^5(X^9)X^{10}$;

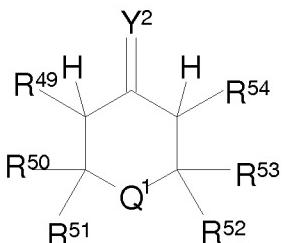
or both D^1 and E^1 together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an optionally substituted phenyl ring:

X^1 represents $CR^1(R^2)(R^3)$, congressyl or adamantyl, X^2 represents $CR^4(R^5)(R^6)$, congressyl or adamantyl, or X^1 and X^2 together with Q^2 to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula IIIa



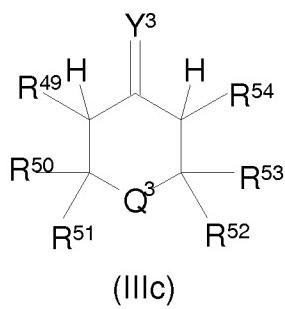
(IIIa)

X^3 represents $CR^7(R^8)(R^9)$, congressyl or adamantyl, X^4 represents $CR^{10}(R^{11})(R^{12})$, congressyl or adamantyl, or X^3 and X^4 together with Q^1 to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X^3 and X^4 together with Q^1 to which they are attached form a ring system of formula IIIb

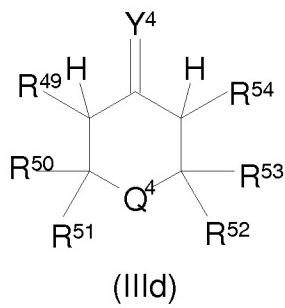


(IIIb)

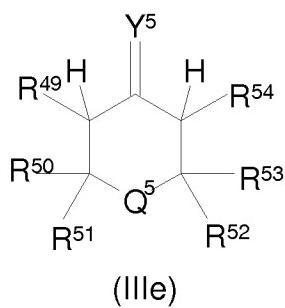
X^5 represents $CR^{13}(R^{14})(R^{15})$, congressyl or adamantyl, X^6 represents $CR^{16}(R^{17})(R^{18})$, congressyl or adamantyl, or X^5 and X^6 together with Q^3 to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X^5 and X^6 together with Q^3 to which they are attached form a ring system of formula IIIc



X⁷ represents CR³¹(R³²)(R³³), congressyl or adamantyl, X⁸ represents CR³⁴(R³⁵)(R³⁶), congressyl or adamantyl, or X⁷ and X⁸ together with Q⁴ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X⁷ and X⁸ together with Q⁴ to which they are attached form a ring system of formula IIId



X⁹ represents CR³⁷(R³⁸)(R³⁹), congressyl or adamantyl, X¹⁰ represents CR⁴⁰(R⁴¹)(R⁴²), congressyl or adamantyl, or X⁹ and X¹⁰ together with Q⁵ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X⁹ and X¹⁰ together with Q⁵ to which they are attached form a ring system of formula IIIe



Q^1 and Q^2 , and Q^3 , Q^4 and Q^5 (when present), each independently represent

phosphorus, arsenic or antimony;

M represents a Group VIB or VIIIB metal or metal cation thereof;

L_1 represents an optionally substituted cyclopentadienyl, indenyl or aryl group;

L_2 represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO, $P(R^{43})(R^{44})R^{45}$ or $N(R^{46})(R^{47})R^{48}$;

R^1 to R^{18} and R^{31} to R^{42} , when present, each independently represent hydrogen, lower alkyl, aryl, halo or Het;

R^{19} to R^{30} and R^{43} to R^{48} , when present, each independently represent hydrogen, lower alkyl, aryl or Het;

R^{49} , R^{54} and R^{55} , when present, each independently represent hydrogen, lower alkyl or aryl;

R^{50} to R^{53} , when present, each independently represent hydrogen, lower alkyl, aryl or Het;

Y^1 , Y^2 , Y^3 , Y^4 and Y^5 , when present, each independently represent oxygen, sulfur or $N-R^{55}$;

$n = 0$ or 1;

and $m = 0$ to 5;

provided that when $n = 1$ then m equals 0, and when n equals 0 then m does not equal 0.

15. (Original) A catalyst system as claimed in claim 14 wherein if both K^1 represents $-A_3-Q^3(X^5)X^6$ and E^1 represents $-A_5-Q^5(X^9)X^{10}$, then D^1 represents $-A_4-Q^4(X^7)X^8$.

16. (Previously Presented) A catalyst system as claimed in claim 12, wherein adamantyl represents unsubstituted adamantyl or adamantyl substituted with one or more unsubstituted C₁-C₈ alkyl substituents, or a combination thereof.
17. (Previously Presented) A catalyst system as claimed in claim 12, wherein 2-phospho-adamantyl represents unsubstituted 2-phospho-adamantyl or 2-phospho-adamantyl substituted with one or more unsubstituted C₁-C₈ alkyl substituents, or a combination thereof.
18. (Previously Presented) A catalyst system as claimed in claim 12, wherein 2-phospho-adamantyl includes one or more oxygen atoms in the 2-phospho-adamantyl skeleton.
19. (Previously Presented) A catalyst system as claimed in claim 12, wherein congressyl represents unsubstituted congressyl.
20. (Previously Presented) A catalyst system according to claim 19 wherein the metal or compound thereof is palladium.
21. (Original) A catalyst system according to claim 20 wherein the palladium is in the metal form.
22. (Previously Presented) A catalyst system according to claim 21, wherein the catalyst system includes in a liquid reaction medium a polymeric dispersant dissolved in a liquid carrier, said polymeric dispersant being capable of stabilising a colloidal suspension of particles of the Group VI or VIIIB metal or metal compound of the catalyst system within the liquid carrier.
23. (Withdrawn - Previously Presented) A process for the carbonylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system as claimed in claim 1.

24. (Withdrawn) A process according to claim 23, wherein the carbonylation of an ethylenically unsaturated compound is performed in one or more aprotic solvents.
25. (Withdrawn – Previously Presented) A process according to claim 23, wherein suitable ethylenically unsaturated compounds include ethene, propene, hexene, vinyl compounds such as vinyl acetates, heptene, octene, nonene, decene, undecene, dodecene, etc up to C₃₀, i.e. having from 2 to 30 carbon atoms, which may be linear or branched, cyclic or uncyclic or part cyclic and in which the double bond may take any suitable position in the carbon chain and which includes all stereoisomers thereof.
26. (Original) A reaction medium comprising one or more reactants, and a catalyst system comprising, or obtainable by combining, at least a Group VIB or VIIIB metal or metal compound, a bidentate phosphine, arsine, or stibine ligand, and an acid, wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.
27. (Previously Presented) A reaction medium comprising one or more reactants, and a catalyst system as claimed in claim 1.
28. (Previously Presented) A reaction medium as claimed in claim 26 wherein the amount of free acid present in the medium is greater than 500ppm.
29. (Withdrawn - Currently Amended) A process comprising using Use of a system comprising, or obtainable by combining:
 - a) a metal of Group VIB or Group VIIIB or a compound thereof,
 - b) a bidentate phosphine, arsine, or stibine ligand, preferably a bidentate phosphine ligand, and

- c) an acid,

wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand, as a catalyst in the carbonylation of an ethylenically unsaturated compound.

30-33. (Canceled)

34. (Original) A catalyst system capable of catalysing the carbonylation of an ethylenically unsaturated compound, said system comprising:

- a) a metal of Group VIB or Group VIIIB or a compound thereof,
- b) a bidentate phosphine, arsine, or stibine ligand, preferably a bidentate phosphine ligand, and
- c) an acid,

wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.

35. (Withdrawn) A process for the carbonylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system, said system comprising:

- a) a metal of Group VIB or Group VIIIB or a compound thereof,
- b) a bidentate phosphine, arsine, or stibine ligand, preferably a bidentate phosphine ligand, and
- c) an acid,

wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.

36. (Original) A complex capable of catalysing the carbonylation of an ethylenically unsaturated compound, said complex obtainable by combining:

- a) a metal of Group VIB or Group VIIIB or a compound thereof,
- b) a bidentate phosphine, arsine, or stibine ligand, preferably a bidentate phosphine ligand, and
- c) an acid,

wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.

37. (Withdrawn) A process for the carbonylation of an ethylenically unsaturated compound with carbon monoxide and a hydroxyl group containing compound in the presence of a complex, said complex as defined in claim 36.